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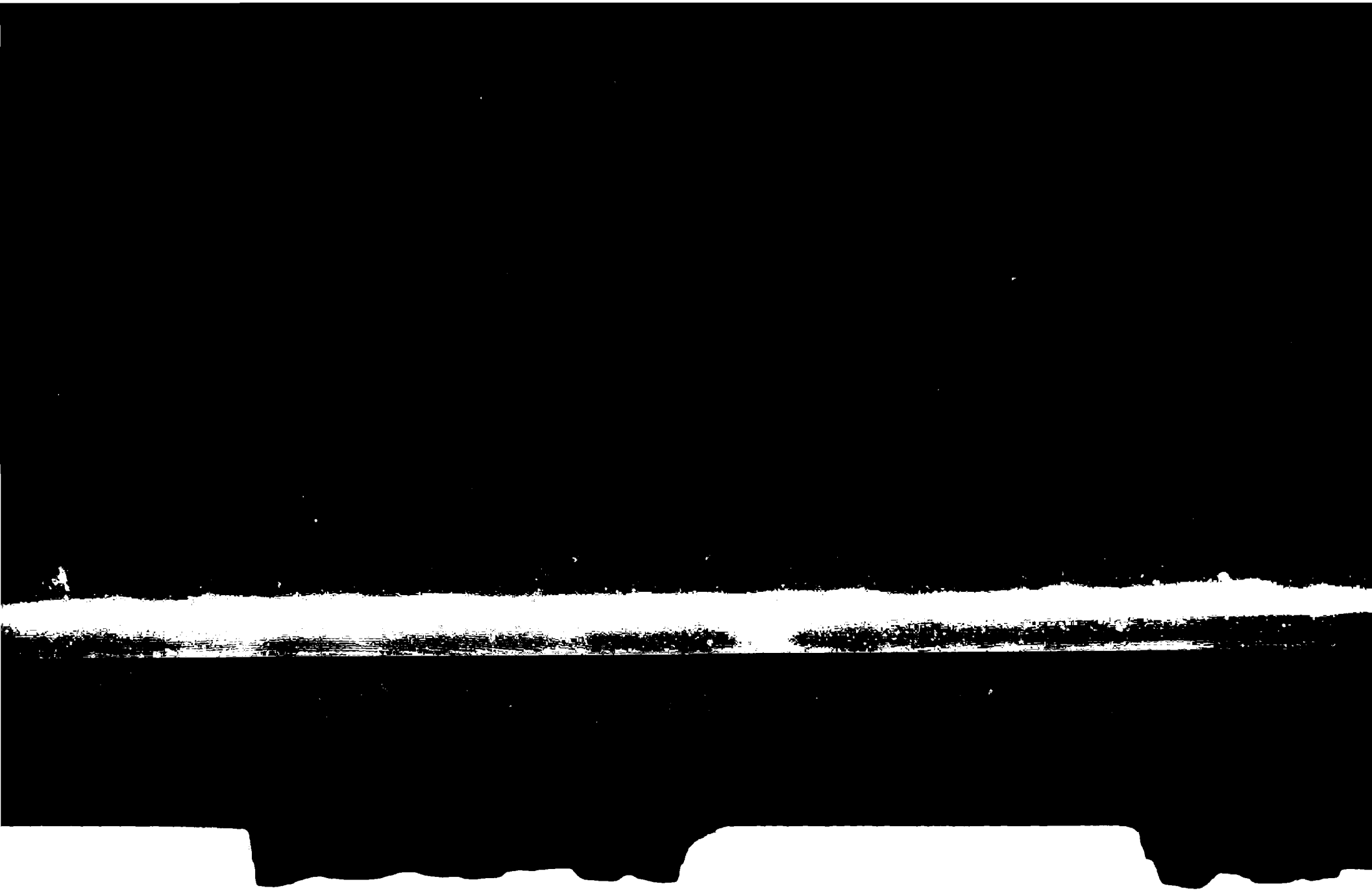

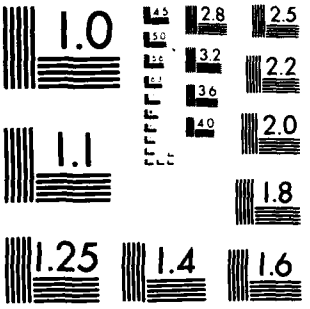

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The overall objective of this research program was to develop theoretical methods for improving the prediction of potential energy surfaces relevant to high energy inelastic collision processes. A "diamotics-in-molecules" approximation for constructing potential energy surfaces of excited electronic states of the prototypical triatomic hydrogen system was developed. A new approximation method was devised to estimate cross sections for inelastic or reactive collision processes from a "rotating rigid rod" model. These semiempirical approaches were complimented by a comprehensive statistical theory for vector properties of collisions, including all angular distributions describing the orientations of the initial and final relative velocity vectors and/or the reactant and product rotational angular momentum vectors.

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FINAL REPORT ON
A THEORETICAL STUDY OF THE ENERGETICS AND DYNAMICS OF HIGH ENERGY INELASTIC COLLISION PROCESSES

Research Conducted in the Department of Chemistry, Harvard University with Support by The Air Force Office of Scientific Research under Contract No. F 49620-80-C-0017.

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APRIL 7, 1984

I. INTRODUCTION

The research pursued under Contract No. F 49620-80-C-0017 was undertaken as a joint project by D.R. Herschbach at Harvard and J.W. Duff, M.B. Faist, and C.E. Kolb at Aerodyne Research, Inc., in Bedford, MA. During the course of the work, Faist moved to the Radian Corporation, in Austin, TX but continued to take part in the project. Although the Contract was awarded to and administered by Harvard, it included a subcontract to Aerodyne Research.

The motivation for this project came from the increasing interest in high energy or hyperthermal ($E_R \sim 0.5$ to 10 eV) inelastic and reactive collisions over the past several years. This interest has been stimulated for at least two reasons. First, the advent of seeded supersonic[1] and arc heated nozzle beams[2-4] as well as fast ion sputtered[5] and laser blowoff[6] beam sources has opened up this previously inaccessible experimental domain. These techniques may be used to produce not only high energy closed-shell species (e.g., rare gases-supersonic nozzle[1]) and monovalent species (e.g., alkali-sputtering[5] and supersonic nozzles and H-atom arc heated sources[2]) but also polyvalent nonmetals (e.g., N-atoms[3] and O-atoms[4] via discharge or arc heated nozzles) and polyvalent metal atoms (heated nozzle and laser blowoff sources). Therefore, a vast range of fundamental experimental information involving hyperthermal inelastic and reactive atom/molecule scattering is becoming accessible to chemical physicists.

Secondly, high energy collisions are of interest from a practical as well as intellectual point of view. For instance, powered missile flight in the Earth's atmosphere above 90 km is generally characterized by very high levels of infrared radiation emanating from the rocket's exhaust plume. The bulk of

this radiation is due to infrared active vibrational/rotational and pure rotational modes of exhaust gases such as CO_2, H_2O, HF, HCl, CO, and NH_3 which have been populated well above local thermodynamic equilibrium (LTE) levels in hyperthermal collisions.[7-8] The high energy nature of exhaust species/atmospheric species (and less predominantly exhaust species/exhaust species) collisions in high altitude rocket plumes is a result of the high velocities (2-6 km/sec) achieved by ballistic missiles at high altitudes.

The development of sophisticated, spaceborne optical tracking and surveillance systems utilizing sensitive infrared sensors has led to an increased interest in sources of missile-related IR signature. Recently, predictive computer codes have been developed at Aerodyne Research to calculate rocket exhaust plume infrared radiation signatures observable to both onboard[9] and offboard sensors.[10] The construction of these codes has required computational advances in nonequilibrium fluid mechanics,[11-13] inelastic energy transfer in hyperthermal collisions,[14-17] and nonequilibrium molecular radiation.[18-21] The most difficult of these calculational efforts is the determination of inelastic excitation cross sections for high energy (>1 eV) collisions between common infrared active exhaust species (e.g., H_2O and CO_2) and atomic oxygen, which is the dominant atmospheric species in most of the upper atmosphere.

In view of the importance of these high energy collision processes it is clear that there is a need for practical theoretical methods to aid in the understanding and prediction of the outcome of such collisions.

II. SUMMARY OF RESULTS

The part of the work conducted at Harvard has produced three published papers.[22-23-24] These deal with:

(1) A "diatomics-in-molecules" approximation for constructing potential energy surfaces of excited electronic states of the prototypical triatomic hydrogen system.

(2) A new approximation method to estimate cross sections for inelastic or reactive collision processes from a "rotating rigid rod" model.

(3) A comprehensive statistical theory for vector properties of collisions, including all angular distributions describing the orientations of the initial and final relative velocity vectors and/or the reactant and product rotational angular momentum vectors.

The work at Harvard also led to a discovery of great promise:

(4) A new and novel "dimensional interpolation" approach to accurate electronic structure calculations. In this, calculations are carried out for the rather simple limiting cases corresponding to one-dimension ($D = 1$) and infinite dimension ($D = \infty$). Interpolation in terms of $1/D$ then provides the electronic energy for the real system ($D = 3$). For the helium atom and other two-electron systems, this method has given remarkably accurate results (error less than 5×10^{-6}) with little labor. If this procedure proves applicable to larger systems, it will revolutionize electronic structure calculations.

The part of the work conducted at Aerodyne has produced two noteworthy results:

(5) A satisfactory theoretical treatment has been achieved which accounts for "ballistic energy transfer." This denotes extremely efficient inelastic

transfer of translational to rovibrational energy observed in hyperthermal collisions of rare gas atoms with alkali halide molecules.[25] A very detailed analysis was carried out for the Ar-Cs-F system, by constructing a potential energy surface by the diatomics-in-molecules method and computing quasi-classical collision trajectories for a wide range of conditions. The results are in excellent agreement with experiment. Thus they serve to account for ballistic energy transfer, a mechanism which had eluded theoretical explanation for over ten years.

(6) A potential energy surface has been constructed for the H + CO system by combining results from ab-initio calculations with spectroscopic data on the HCO radical. Trajectory calculations employing this surface were carried out to compare with the exceptionally good experimental results recently obtained for hyperthermal inelastic collisions of H + CO. Excellent agreement was found for the data on translational-to-vibrational energy transfer.[26] Agreement with the data on vibrational-to-rotational transfer is also good in an average sense. However, the calculations failed to predict a pronounced bimodal structure observed in the energy transfer,[27] and this appears to be due to inaccuracy in an important region of the surface.

Three papers describing the work outlined in (1), (2), and (3) are attached to this report. Papers presenting the work of (4), (5), and (6) are still in preparation. The funds provided by the Contract (and its subcontract) were fully expended.

III. A REMARK

Theoretical methods for practical calculations of collision properties are now available, but cannot be usefully applied because of the lack of sufficiently accurate potential energy surfaces. Methods to compute such accurate surfaces thus deserve the highest priority if progress is to be made in this area.

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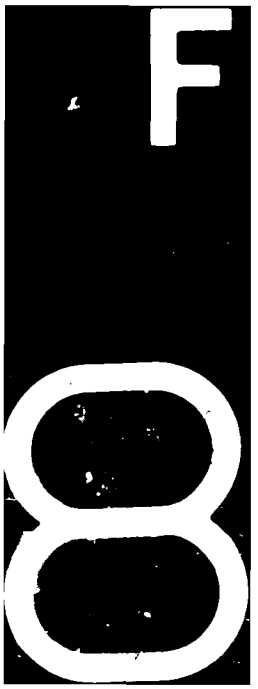
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